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The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

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13. ABSTRACT (Maximum 200 words)

Cellulose is the most abundant form of living biomass on earth. It has been estimated that the annual photosynthetic production of cellulose is well over 1.5×10^{12} tons per year. This material represents an extraordinary amount of stored chemical energy. Unfortunately, the form of this stored energy (solid cellulose) is not directly accessible to modern military systems. To utilize this energy requires the conversion of solid cellulose into a compatible liquid fuel. Since modern military systems operate predominately on hydrocarbon based fuels, what is needed is a clean, facile, energy efficient, cost effective, and "green" method to convert cellulose into hydrocarbon fuels. In this effort we are investigating the application of ionic liquids to the conversion of cellulose to hydrocarbons. To accomplish this we are evaluating the dissolution and subsequent catalytic depolymerization of cellulose to glucose and related simple sugars in a single ionic liquid. In addition, we are studying the catalytic reduction of glucose to hydrocarbons in an ionic liquid solvent, and, finally, we are looking toward combining the dissolution, depolymerization, and reduction processes into a single ionic liquid based process.

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Enclosure 1

Annual Report

I. Abstract

Cellulose is the most abundant form of living biomass on earth. It has been estimated that the annual photosynthetic production of cellulose is well over 1.5×10^{12} tons per year. This material represents an extraordinary amount of stored chemical energy. Unfortunately, the form of this stored energy (solid cellulose) is not directly accessible to modern military systems. To utilize this energy requires the conversion of solid cellulose into a compatible liquid fuel. Since modern military systems operate predominately on hydrocarbon based fuels, what is needed is a clean, facile, energy efficient, cost effective, and "green" method to convert cellulose into hydrocarbon fuels. In this effort we are investigating the application of ionic liquids to the conversion of cellulose to hydrocarbons. To accomplish this we are evaluating the dissolution and subsequent catalytic depolymerization of cellulose to glucose and related simple sugars in a single ionic liquid. In addition, we are studying the catalytic reduction of glucose to hydrocarbons in an ionic liquid solvent, and, finally, we are looking toward combining the dissolution, depolymerization, and reduction processes into a single ionic liquid based process.

II. Technical Section

Technical Objective

Ionic liquids have recently been shown to simply and effectively dissolve cellulose,[1] ionic liquids are also well known to be excellent media for low temperature catalytic processing of organic materials,[2] and ionic liquids are easily separable from hydrocarbons due to their immiscibility. <u>The main goal of this project is to demonstrate the feasibility of converting cellulose to hydrocarbon fuels using ionic liquids has solvent and catalytic medium.</u>

Technical Approach

Our approach to this effort has been to systematically investigate the use of ionic liquids in the conversion of cellulose to hydrocarbon products. We have divided this effort into the following tasks listed below and shown schematically in Figure 1.

Project Tasks

<u>Task 1:</u> Evaluation of the dissolution of cellulose in ionic liquids and optimization of the ionic liquid solvent for the overall conversion process.

<u>Task 2:</u> Investigation of the catalytic hydrolysis/depolymerization of cellulose in ionic liquid solvents.

<u>Task 3:</u> Examination of the catalytic reduction of glucose to hydrocarbons in an ionic liquid solvent.

<u>Task 4</u>: Assessment of the potential of combining the dissolution, depolymerization, and reduction processes into a single ionic liquid based process.

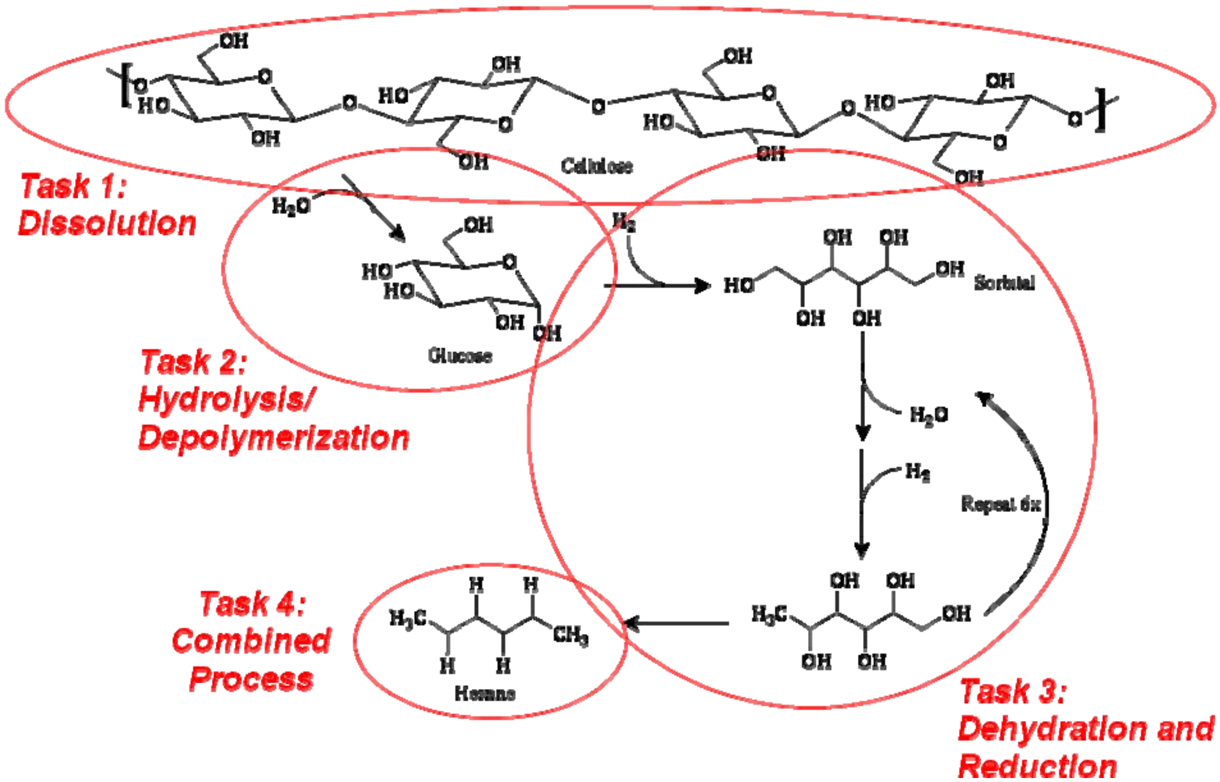


Figure 1. Schematic of the overall project and tasks

Task 1 will be accomplished by evaluating the dissolution and solvation of cellulose in ionic liquids using a variety of experimental methods. Using this information we will design and synthesize ionic liquids with optimal properties for the dissolution and processing of cellulose. Task 2 will be accomplished by developing depolymerization catalysts for use in the ionic liquid/cellulose solutions. We will then evaluate the effectiveness of these catalysts in producing simple sugars (e.g., glucose) from dissolved cellulose. We will accomplish Task 3 by evaluating the reduction/dehydration of simple sugars using existing catalyst systems. We also design and test new ionic liquid based reduction/dehydration catalysts for this step of the process. Finally, Task 4 will be attempted once significant progress has been made in the first three tasks. In this effort we will work at combining the dissolution, depolymerization, and reduction processes into a single "one-pot" ionic liquid based process. Furthermore, we will exploring the feasibility of a carrying out this overall conversion as a continuous process (vice a batch process).

Progress Statement Summary

In this effort we are studying the ionic liquid based transformation of cellulose biomass to hydrocarbon fuels. Over the past year we have used small angle neutron scattering to characterize the structure of cellulose dissolved in an ionic liquid. We have found that the cellulose exists as a large flexible aggregate of 5-7 polymer chains. We have characterized the solubilities of the expected cellulose depolymerization products in the ionic liquids, and we have evaluated the separation of these products from the ionic liquids using common organic solvents. We have synthesized and characterized several novel ionic liquid depolymerization catalysts, and we have begun testing these catalysts on cellulose/ionic liquid solutions. Initial results show positive Benedict's tests for reducing sugars indicating the successful depolymerizaiton of cellulose.

Progress

Over the past year we have focused much of our effort on Tasks 1 and 2. We have made significant progress in the understanding of the cellulose dissolution process, we have synthesize some novel ionic liquid depolymerization catalysts, and, most importantly, we have obtained initial positive results for the depolymerization of cellulose in ionic liquids. We have performed some initial studies relevant to Task 3, and we have yet to direct our efforts towards Task 4.

Task 1 – Evaluation of the dissolution of cellulose in ionic liquids and optimization the ionic liquid solvent for the overall conversion process.

In an effort to understand the solvation of cellulose in ionic liquids we have investigated cellulose/ionic liquid solutions using small angle neutron scattering (SANS).[3] Small Angle Neutron Scattering (SANS) can provide information on the size, shape, and rigidity of a polymer in solution. SANS requires the use of deuterated solvents to minimize the hydrogen cross section, so to carry out these experiments we have synthesized the per-deuterated ionic liquid, 1-ethyl-d_5-3-methyl-d_3-imidazolium chloride Figure 2 shows the Kratky plot of SANS data for solutions of cellulose and silk in the 1-ethyl-d_5-3-methyl-d_3-imidazolium chloride ionic liquid. The absence of a plateau at small-Q indicates that cellulose is present as 300 – 500 nm aggregates in the ionic liquid. This would indicate that cellulose exists as globular clusters of 5-7 strands instead of as single strands as was originally assumed. The inflection at mid-Q in the SANS data indicates that the persistence length (length of rigid segments) of the cellulose is ~3 nm; thus indicating that the cellulose if highly flexible in the ionic liquid. It must be noted that the SANS experiments were limited to dilute solutions (~1 mg/mL), so we were not able to evaluate the potential impacts of highly concentrated solutions on the solvation of the cellulose. In an effort to confirm and expand upon the results of the SANS studies we have initiated dynamic light scattering experiments on similar cellulose/ionic liquid solutions.

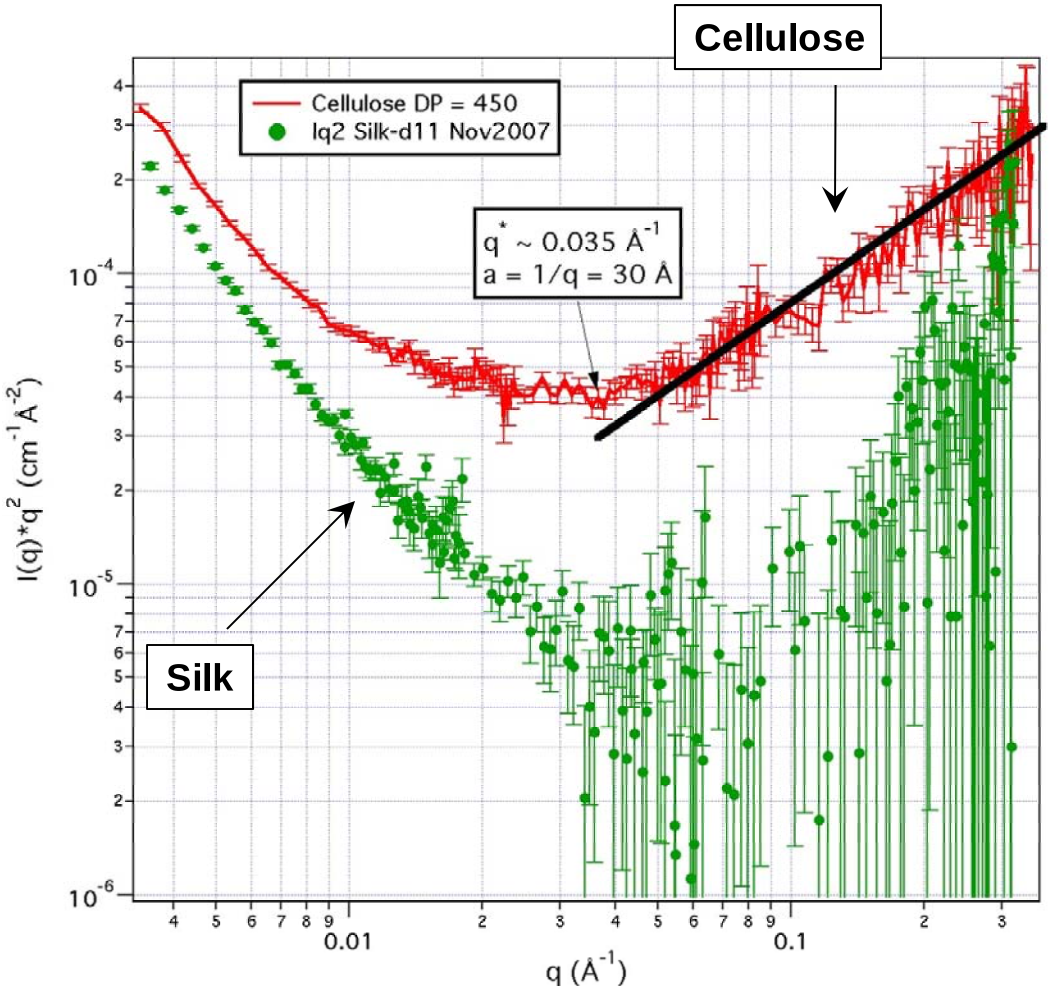


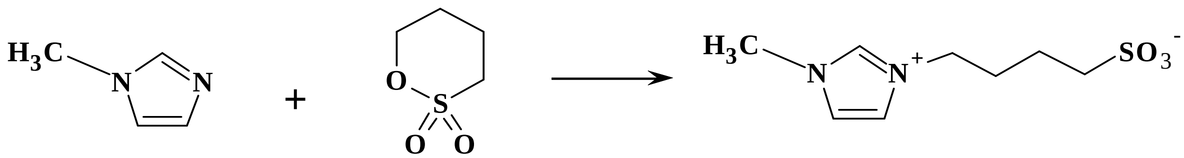
Figure 2. The Kratky plot of small angle neutron scattering data for Cellulose and Silk in the 1-ethyl-d_5-3-methyl-d_3-imidazolium chloride ionic liquid. Measurements were carried out at 90 °C

Task 2 - Investigation of the catalytic hydrolysis/depolymerization of cellulose in ionic liquid solvents.

Ionic liquids possess the unique ability to dissolve cellulose without degrading or derivatizing the cellulose.[4] The dissolution of cellulose opens up the polymer matrix which should allow an acid catalyst to react with the entire polymer chain facilitating the depolymerization to glucose. We have studied the solubility of glucose, fructose, and sorbitol (likely products of the cellulose conversion) in the ionic liquids used to solubilize the cellulose. We have found each of these sugars to have high solubilities in the ionic liquids (> 5 wt %). More importantly we found that each of these sugars can be selectively extracted from the ionic liquid/cellulose solution using common organic solvents such as ethers (e.g., diethyl ether) and hydrocarbons (e.g., n-hexane).

We have initiated the synthesis and characterization of a family of acidic ionic liquid depolymerization catalysts. The basis of the synthesis is the reaction of 1,3-alkyl sultones with

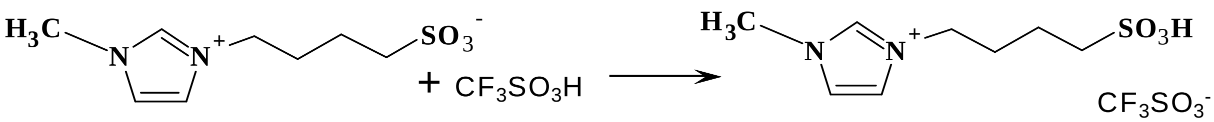
1-methylimidazole to form a zwitterion.[5] Equation 1 shows this reaction for the 1,3-butane sultone. Through use of sultones of varying alkyl lengths we can synthesize zwitterions with varying carbon spacers between the SO_3^- group and the imidazolium ring. We have currently synthesized 3 and 4 carbon spacers, and we are in the process of synthesizing zwitterions with 5 – 10 carbon spacers.



(1)

1

The zwitterion is converted to an ionic liquid by reacting it with a strong acid such as trifluoromethanesulfonic acid, CF_3SO_3H. An example of this reaction with zwitterion ***1*** to produce ionic liquid acid catalyst ***2*** is shown in Equation 2.



(2)

2

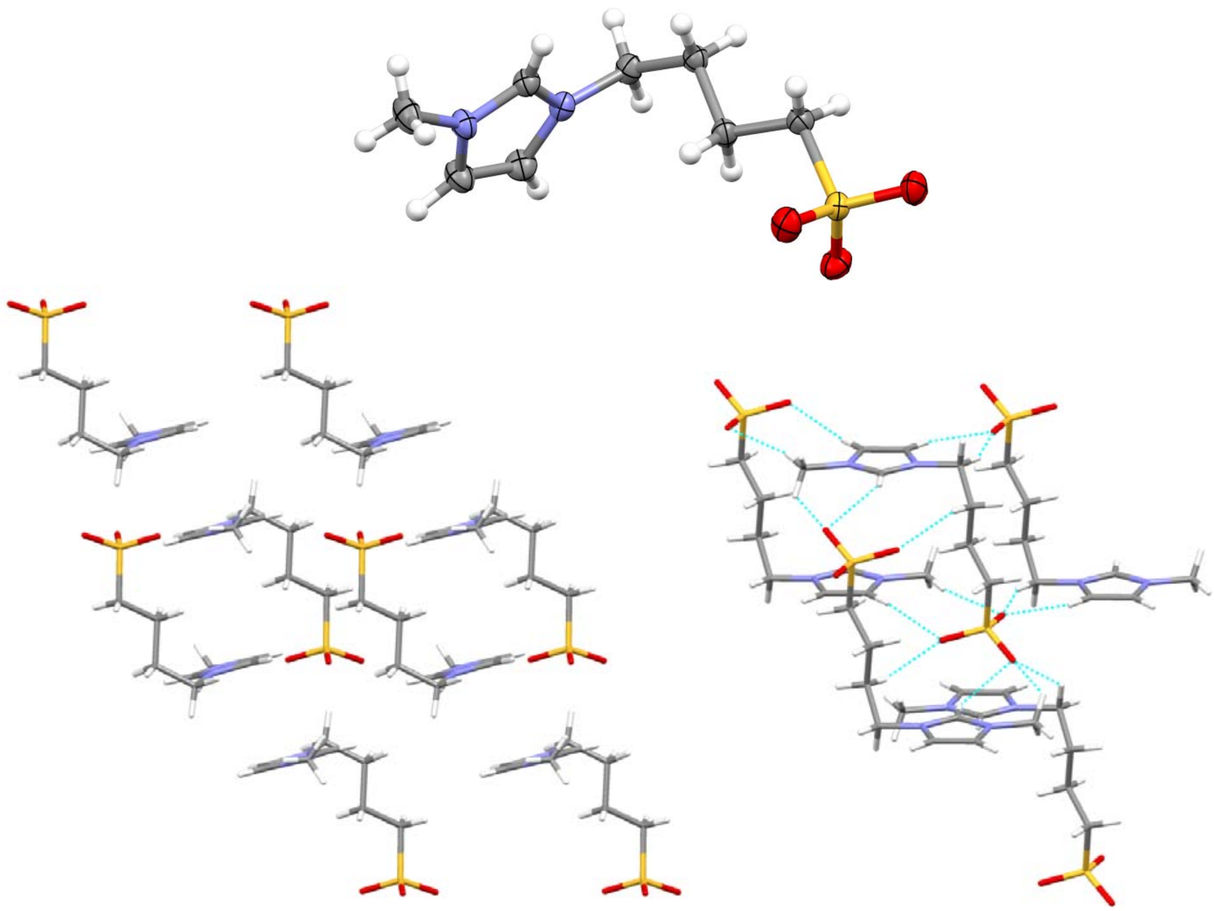


Figure 3. Crystal packing of Zwitterion ***1***.

Figure 3 shows the crystal structure of the zwitterion ***1***, and Table 1 gives the crystallographic parameters for this structure. The close contacts and packing illustrate the strong coulombic interactions between the cationic and anionic parts of the zwitterion. Protonation of the zwitterion (Equation 2) and the introduction of an anion results in a disruption of these strong coulombic interactions and the formation of an ionic liquid.

Table 1. Crystallographic Parameters for the crystal structure of Zwitterion ***1***.

Chemical Formula	$C_4H_{14}N_2O_3S$
Formula Weight	170.23
Crystal System	Triclinic
Space group	P-1 (No. 2)
a (Å)	8.4553(3)
b (Å)	8.4601(3)
c (Å)	8.7558(3)
α (°)	66.6200(10)
β (°)	66.2540(10)
γ (°)	70.6790(10)
V (Å^3)	515.21(3)
Z	3
D_{calc} (g cm^{-3})	1.646
μ(MoKα) (mm^{-1})	3.841
F(000)	276
T (K)	173
$\theta_{min-max}$ (°)	5.80-65.37
Reflections measured	3665
Independent reflections, R_{int}	1632, 0.0168
Observed data [$I > 2\sigma(I)$]	1632
No. parameters	184
R^a, wR_2^b, GOF^c	0.0326, 0.0860, 1.081

We have initiated studies with our new ionic liquid depolymerization catalysts to determine their effectiveness in the conversion of cellulose into simple sugars. These experiments have been carried out on cellulose dissolved in the 1-ethyl-3-methyl-imidazolium acetate ionic liquid. Our first level evaluation of successful depolymerization was done using Benedict's test.[6] Benedict's test is a classical organic test for reducing sugars (e.g., sugars with free aldehyde or ketone groups). The Benedict's test involves the reduction of copper (II) to copper (I) by a reducing sugar and the subsequent precipitation of copper (I) oxide (Equation 3). The copper (I) oxide is a red-brown precipitate. When this red-brown precipitate is in the presence of the unreacted blue copper (II) the resulting solution will appear from green to brown when going from low to high concentrations of reducing sugar, respectively.

$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H \;+\; Cu^{2+} \xrightarrow{\Delta} R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O^{-} \;+\; Cu_2O(s) \qquad (3)$$

Figure 4 shows the results for the Benedict's test of a series of reactions in 10 wt % cellulose in ionic liquid and varying amounts of ionic liquid acid catalyst ***2*** (C, D, and E). In each case, a positive Benedict's test was obtained indicating the presence of reducing sugars. Furthermore, the color of the Benedict's test indicates that increasing catalyst concentration gave a higher concentration of reducing sugars. To ensure that the catalyst and/or ionic liquid were not responsible for the positive Benedict's test, we also did a series of blank experiments (Figure 4), but in no case did we obtain a positive test.

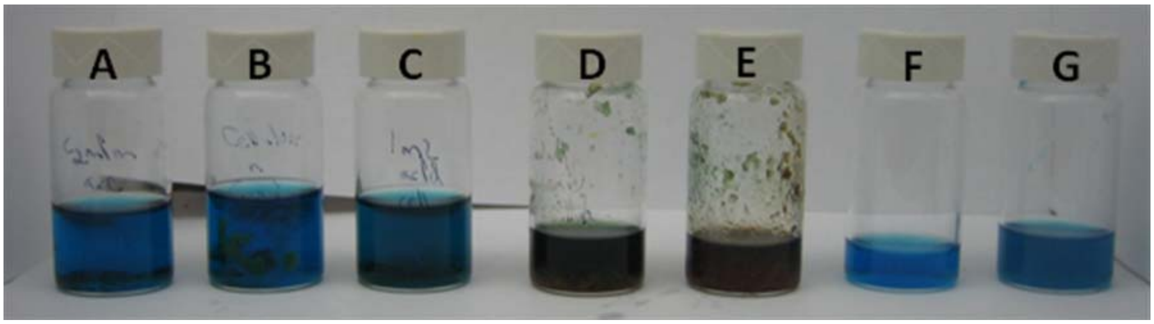


Figure 4. Initial Results for the Depolymerization of Cellulose. Results of Benedict's test for;

A. Pure IL
B. 10% cellulose regenerated from IL
C. 1 mL catalyst reacted with 10 mL of 10 wt % cellulose in IL
D. 2 mL catalyst reacted with 10 mL of 10 wt % cellulose in IL
E. 3mL catalyst reacted with 10 mL of 10 wt % cellulose in IL
F. 1mL catalyst in microcrystalline cellulose
G. 1mL catalyst reacted with 10 mL of 10 wt % cellulose in IL (no heating)

These results clearly demonstrate successful depolymerization of cellulose to simple sugars in the ionic liquids! However, they do not provide any quantitative information as to the overall yield of the reaction, and they give us no information on the composition of the product mixture. As such we are in the process of confirming our initial results and evaluation product mixtures using several chromatographic methods (e.g., HPLC, and LC-MS). In addition, we are working on quantifying the conversion using a modification of the Benedict's test which involves the titration of the unreacted copper (II). We are also looking to further characterize the depolymerization reaction by looking at the effects of cellulose concentration, catalyst concentration, reaction temperature, reaction time, and mixing.

Task 3 - Examination of the catalytic reduction of glucose to hydrocarbons in an ionic liquid solvent.

We have initiated studies on the stepwise reduction of glucose in an ionic liquid. However, we have made limited progress on this part of the effort. We are studying the reduction/dehydration of sorbital in the ILs. The current proposed path is to use metal catalysts and hydrogen. The challenge has been to accomplish this reduction without reducing the IL. At this time we have not had much success. There are several potential solutions to this problem in the reduction process. We could look at homogeneous catalysis to see if we can direct the reduction process specifically at the sorbitol, or we could change our IL to one with a fully reduced cation (e.g., pyrollidinium).

We have evaluated the miscibility of expected hydrocarbon products in the current ionic liquids being used in the generation and reduction of glucose and we have found them to be very immiscible. However, hydrocarbons with hydroxyl groups (e.g., expected partial reduction products of glucose) tend to be relatively miscible in the ionic liquids.

Task 4 - Assessment of the potential of combining the dissolution, depolymerization, and reduction processes into a single ionic liquid based process.

We have did not carry our any work specifically directed at this task over the past year.

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